

THE USE OF OPTICAL ACTIVITY MEASUREMENTS IN OIL SHALE PROCESSING

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INTRODUCTION

Shale oil reserves are more than three and one-half times the amount of world petroleum reserves (1). But because of overburden, most of the reserves cannot be mined conventionally; an in-situ process must be used for oil recovery. The in-situ process has advantages over aboveground, conventional processes because transporting or crushing the shale is unnecessary before retorting; and spent shale disposal is no problem after retorting. But a disadvantage is the difficulty of monitoring the relatively deep underground conversion changes. One developing method for following these changes is optical activity measurements on the shale oil during its production because we know the optical activity of shale oil decreases with increasing heating rate (2). Shale oil is optically active because oil shale contains optically active biological markers derived from life forms existing during the formation of the shale deposit (3). Known biological markers--steranes, diterpanes, gammacerane, and perhydro-8-carotene--are reduction products from diagenesis of former living systems. Despite the rigors of heating, in most retorting systems these optically active molecules survive in sufficient quantities to allow their detection with a sensitive spectropolarimeter. These measurements show promise in studying large-scale field retorting systems.

This study at the Laramie Energy Research Center (LERC) shows examples of optical activity measurements in a controlled-state retort system, in the Site 9 in-situ field experiment, located at Rock Springs, Wyo., and in differing retorting systems using Green River, Antrim, and Moroccan oil shales.

EXPERIMENTAL

Optical activity measurements were made on the saturate fraction from the shale oil and bitumen, as described in detail earlier (2). Briefly, 1/2 g of dried oil in a 50-ml beaker was dissolved in 20 ml of cyclohexane (Burdick and Jackson Laboratories, Inc.). The solution was cooled to 0°C in a circulating cold bath, and 10 ml of 15 percent phosphorous pentoxide in sulfuric acid was slowly added with stirring. Stirring was continued for 1 hour, then the mixture was transferred and centrifuged for 1/2 hour at 3000 RPM. The cyclohexane layer was drawn off, and the bottom layer was twice more mixed with 10 ml of cyclohexane and centrifuged. Then the combined solution was decolorized by passing it over 10 gm of "powdered" silica gel (Baker, 60-200 mesh), eluting with cyclohexane, and collecting the first 10 ml of solution. The solution was evaporated under nitrogen to 20 ml. The optical activity was determined on this solution in the ORD mode with a Jasco J-20 spectropolarimeter. Optical activity data were determined in the 300- to 600-nm wavelength range and the solution was evaporated to dryness to determine the total saturates. The optical activity data were calculated based upon the amount of total saturates.

Shale oils and bitumens from an interrupted, controlled-state retort experiment (4) were analyzed. Green River formation oil shale, 1/8-to 1/2-in. particle

size, was packed into a vertical 3-in. stainless steel pipe and was externally electrically heated in 6-in. increments at a 2°F-per-minute heating rate with a zone travel rate of 3 in. per hour. Produced oil flowed downward with assistance from a nitrogen sweep gas. After approximately half of the shale column had reached a temperature of 1000°F (about 36 hours), the experiment was stopped; the pipe was cooled with water and cut into 24 6-in. segments. The shale samples from the 24 segments consisted of 14 spent-shale samples and 10 samples of oil-wet shale, with varying temperature exposures from 730°F to ambient. The oil-wet shale samples were rinsed with cyclohexane to recover the surface oil samples. The rinsed samples were dried at room temperature, crushed to 200 mesh, and Soxhlet extracted for 48 hours with cyclohexane to obtain the bitumen samples. The surface oil and bitumen samples were prepared and analyzed for optical activity as described.

Optical activity analyses were made on several retorting systems using the described method. Nine composite samples of shale oil were analyzed, representing 6 months of operation at the LERC Site 9 in-situ field experiment (5). Shale oils were analyzed from the bench-scale controlled-state retort system; from five aboveground, semi-works retort systems; and from two large-block systems.

RESULTS AND DISCUSSION

Only data from the 450-nm wavelength are presented in Figures 1 and 2 for ease of interpretation. Shale oil optical activity changes as the retort heating rate changes (2). And since heating rate consists of two components, temperature and time, optical activity changes should be related to each of these components. Data from analysis of oils and bitumens from the interrupted controlled-state retort are shown in Figure 1. Oils rinsed from the surface of the cooler shale have, except for samples 15 and 24, a specific rotation of about 4 units. Sample 15, having been exposed to the hottest temperature (730°F), shows only a trace of activity; and the last sample, 24, has about nine degrees of rotation, possibly because the cooler end of the retort causes dilution by accumulations of saturates. The wavelike distribution of the data is probably real in that it is well within the testing limits. The receiver oil, from about one-half of the total charged shale, shows an optical rotation of about four degrees, approximating the values from the surface oils.

The optical activity of the bitumens extracted from the partly retorted shale (samples 15 to 19) and from the unretorted shale (samples 20 to 24) is also shown in Figure 1. A smooth curve evolves, proceeding from sample 20 to 15, indicating that the effect of heat on the shale produces a uniform loss of optical activity in the bitumen. An induction period before the retorting of the shale (estimated to occur at about 400°F) occurs in the low-temperature loss of activity in samples 19 to 17. Sample 19 has a rotation of approximately 12 degrees; number 17 approximately 10 degrees. This 2-degree difference apparently results from increasing the temperature from 110 to 190°F over a 4-hour period. Samples 15 and 16 reflect a rapid loss of activity as the shale becomes heated to retorting temperature with subsequent emergence of oil. The rapid increase in optical activity from sample 20 to 23 cannot be satisfactorily explained at this time but approaches the optical activity of Green River natural bitumen--typically 30 units.

Oils from the Site 9 in-situ field experiment were analyzed for optical activity. The results in Figure 2 show that the oils produced during the first part of the 6-month experiment were more optically active than those in the second half. The lower optical activity in the second half of the experiment probably results from a different thermal history. The results may reflect change in the air-injection system when on the 60th day the injection well was changed from well No. 1 (located at the center of the site) to well No. 10 (located nearer the edge of the site), thereby moving the air injection closer to the moving combustion front, possibly further decomposing previously accumulated oil. The general decrease in

optical activity for all the composite oils indicates that after 6 months of production a "steady state" oil was not produced. The general indication of oil decomposition is not evident in 10 other physical or chemical tests, as shown in Table 1. Traditional indications of oil thermal decomposition such as increasing olefin, aromatic, and naphtha contents or decreasing viscosity and pour point, are not unequivocally present. In some instances, as in olefin content, the last four samples are in opposition to the optical activity data by having generally lower amounts of olefins--less oil decomposition. The optical activity data indicate that the last four samples are decomposed the most.

TABLE 1. - Properties of Site 9 composite oils

Property	Sample number								
	1	2	3	4	5	6	7	8	9
Naphtha, percent*	9	6	6	8	10	10	11	12	14
Olefins, percent in naphtha	36	32	25	19	--	19	14	27	9
Olefins, percent in light distillate	22	37	38	35	--	15	13	12	33
Paraffins, percent in naphtha	43	17	51	57	--	54	59	45	63
Paraffins, percent in light distillate	22	46	49	52	49	52	57	56	38
Aromatics, percent in naphtha	21	22	24	24	--	27	27	28	28
Aromatics, percent in light distillate	35	17	13	13	34	33	30	32	29
Residuum, percent*	6	6	6	7	5	4	5	8	7
Viscosity, SUS 100°F	53	58	57	53	50	46	47	56	45
Pour point, °F	35	40	40	45	45	40	45	40	35
Optical activity $[\alpha]_{450}^{25}$	3.2	2.1	1.9	1.8	1.6	0.8	0.6	0.3	0.2

*Determined by simulated distillation

Oils from different retorting systems were analyzed for optical activity to determine the possibility of observing basic differences among retorting systems. The results in Figure 3 show that differences are observable. Data from the entire 300- to 600-nm range are presented in Figures 3 and 4 for more comprehensive data evaluation. Generally, the optical activity data may be categorized into three groups. First, the least decomposed oils are derived from the controlled-state system where small shale particles, gravity flow, and nitrogen gas sweeping allowed the produced oil to escape from the shale easily thereby minimizing secondary oil decomposition. The second group of oils was produced from large, aboveground,

semi-works retorts with relatively medium shale particles (1 to 6 in.) and moderate capability for the oil to escape the shale. The third group of oils was produced from LERC's aboveground, simulated in-situ 150-ton retort and the Site 9 in-situ system that may be characterized as large-block systems; therefore, slow escape of oil from the shale would be probable. Slow escape of oil would presumably cause considerable decomposition.

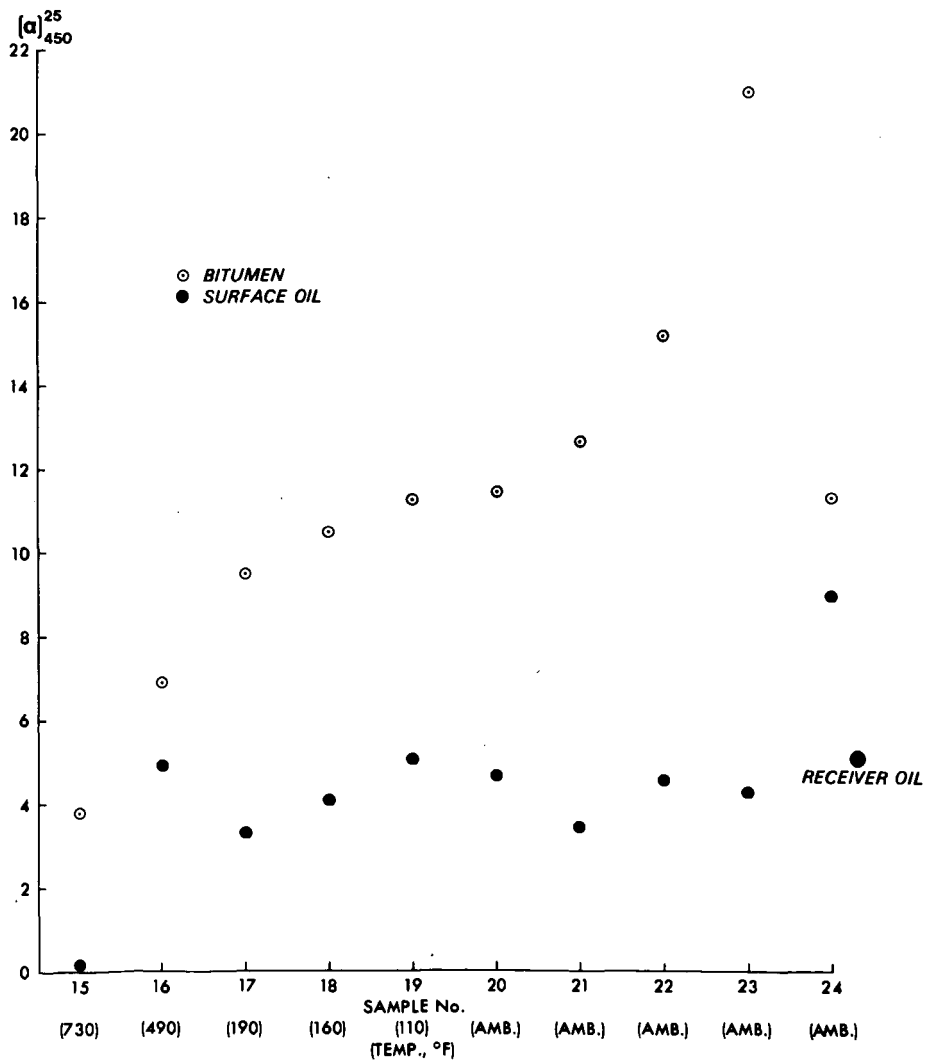
Optical activity comparisons were made among oils produced in the LERC 10-ton retort using Green River, Antrim, and Moroccan shales. Figure 4 shows the Green River shale oil to be the most optically active by at least a factor of 2 at all wavelengths. The Antrim and Moroccan shale oils have essentially identical activity probably reflecting the amounts of optically active components in the original shales. These shales have, interestingly, a marine origin, while the Green River shale has a nonmarine origin.

SUMMARY

Optical activity measurements of shale oils allow insights into retorting conditions that are not observable by traditional analytical methods. With a bench-scale retort, a low-temperature induction period in the shale before retorting can be observed. The retorting phase itself may be observed by following changes in bitumen and in surface oil optical activity. Optical activity data from Site 9 composite oils, representing 6 months of production, reflect two distinct retorting phases of the experiment. The second, lower optically active phase, may have resulted from secondary degradation of previously accumulated oil. Despite 6 production months, a "steady state" oil was not produced. Optical activity data from 10 different retorting system oils show decreasing optical activity with increasing shale size.

REFERENCES

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**FIGURE 1. - OPTICAL ACTIVITY OF SATS. (450nm.).
INTERRUPTED CONTROLLED STATE RETORT.**

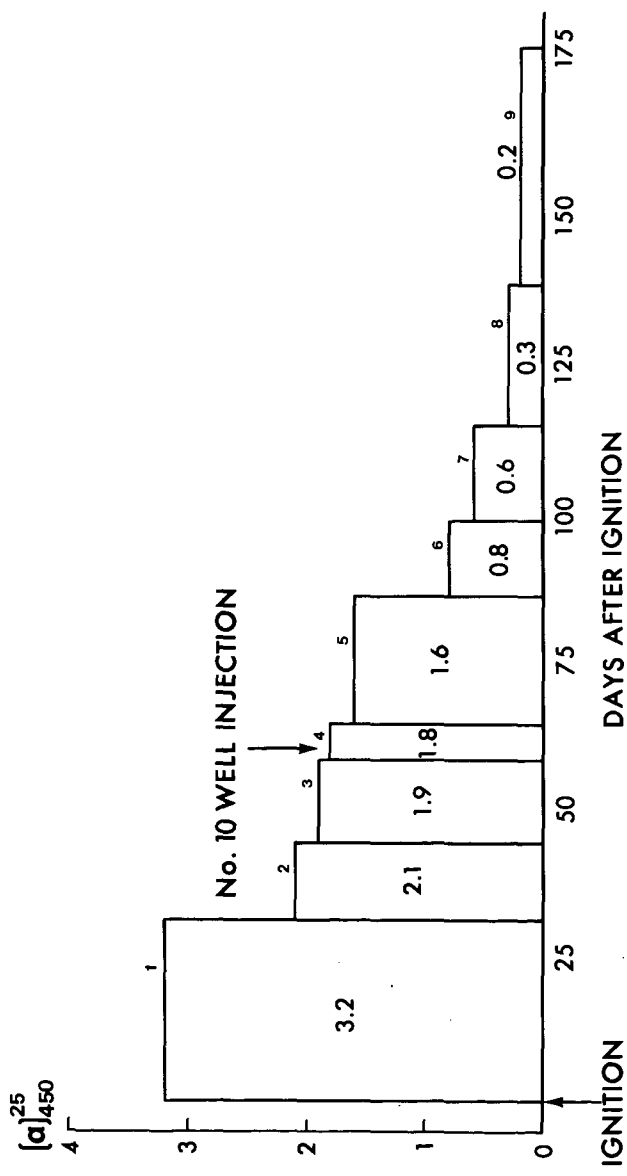


FIGURE 2. - OPTICAL ACTIVITY OF SITE 9 COMPOSITE OILS.

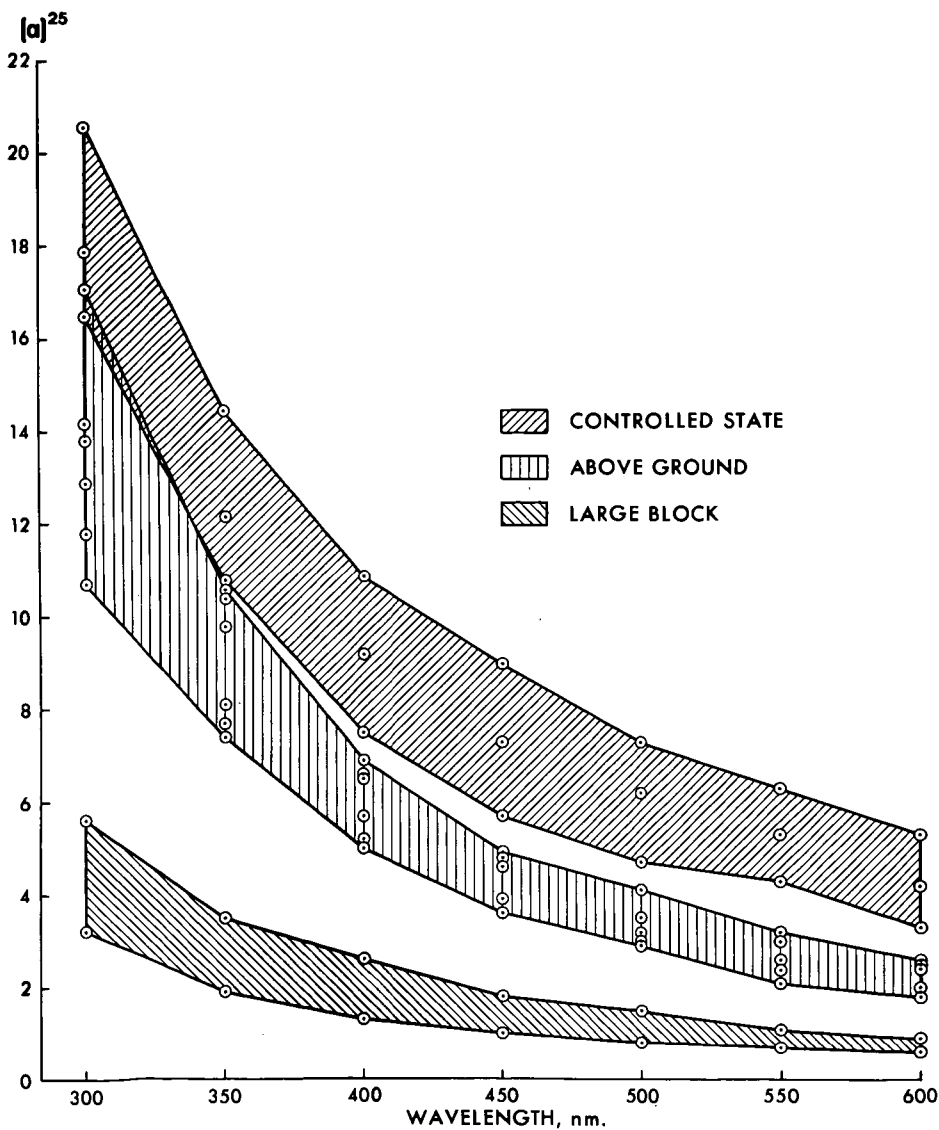


FIGURE 3. - OPTICAL ACTIVITY OF OILS FROM DIFFERENT RETORTS, GREEN RIVER FORMATION SHALES.

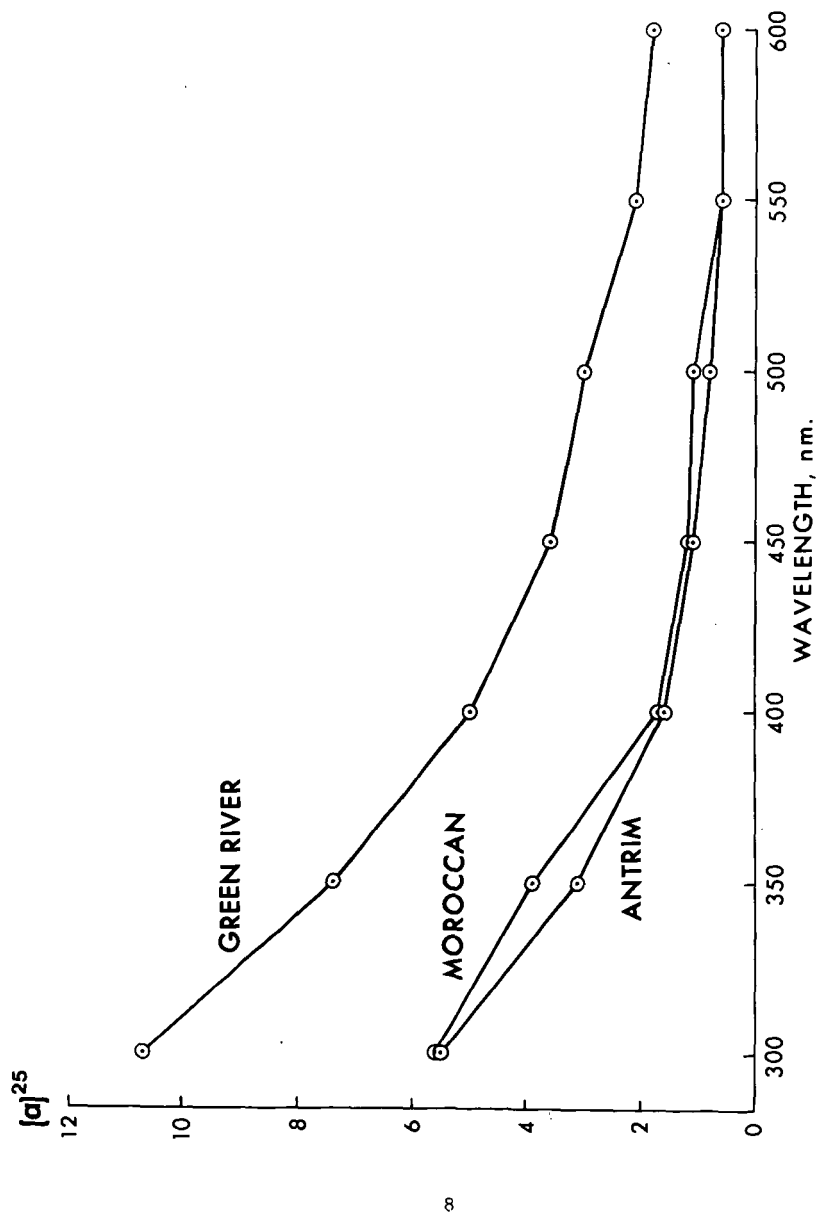


FIGURE 4. - OPTICAL ACTIVITY OF GREEN RIVER, ANTRIM AND MOROCCAN SHALE OILS, 10 TON RETORT.